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(54) Ag ALLOY REFLECTION FILM FOR PLANAR DISPLAY DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an Ag alloy reflection film for a planar display device which has improved high reflectivity, environmental influence, chemical resistance and adhesion with a substrate.

SOLUTION: The Ag alloy reflection film for a planar display device has a composition containing one or more kinds of elements selected from Ce, Nd, Sm, Gd, Tb and Dy by 0.2 to 5 at(atomic).%, and the balance substantially Ag. Additionally, one or more kinds of elements selected from Ti, V, Nb, Cr, Mo and Mn can be incorporated therein by 1 to 10 at.%.

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**CLAIMS**

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[Claim(s)]

[Claim 1]An Ag alloy system reflection film becoming a 0.2-5at% implication and a remainder real target from Ag in total about one or more sorts of elements chosen from Ce, Nd, Sm, Gd, Tb, and Dy.

[Claim 2]one or more sorts of elements chosen from Ti, V, Nb, Cr, Mo, and Mn -- 1 - 10at% -- the containing Ag alloy system reflection film according to claim 1.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]In plane display devices, such as a liquid crystal display, a plasma display panel (following, PDP), a field emission display (following, FED), and electroluminescence (following, EL), for example this invention, It is related with the Ag alloy system reflection film in which high optical reflectance and corrosion resistance are demanded.

[0002]

[Description of the Prior Art]Conventionally, the transmissive liquid crystal display of the liquid crystal display which has high display quality by building in a light source (lamp) as a back light, and glaring from the back was common. However, there was a problem said that the power consumption of transmissive liquid crystal display of a back light is large, and a hour of use becomes short as a Personal Digital Assistant of a battery drive. For this reason, development of the reflective liquid crystal display which uses outdoor daylight efficiently and does not use a back light fundamentally is performed in recent years. Many aluminum or the aluminum alloy thin films which are an element with high reflectance of a light region have been used for the reflection film used for such a reflection type display also in metal.

[0003]The reflection film is asked for the flat reflection property in the high reflection and light region which are called a paper white in recent years for display upgrading of a liquid crystal display. For this reason, Ag whose reflectance is higher than aluminum attracts attention.

[0004]

[Problem(s) to be Solved by the Invention]In the case of above-mentioned aluminum system reflection film, a hillock etc. occur in the heating process in the manufacturing process of a liquid crystal display, and there is a problem to which reflectance falls with grain growth. For this reason, the aluminum alloy which adds January the 15th of the lunar calendar matter for

corrosion resistance which is transition metals, such as Ti and Ta, is used for aluminum for control of the above-mentioned hillock or grain growth. The reflectance reduction at the time of liquid crystal display manufacture can be controlled with this aluminum alloy. However, there is a problem to which the reflectance of a raw material itself falls.

[0005]On the other hand, in the case of Ag reflection film with high reflectance, there is a problem that the adhesion over glass and the plastic which are the substrates for liquid crystal displays is low, and peeling arises in a process. This adhesion originates in a low thing, a film condenses by the heating process at the time of manufacture of a display, etc., and reflectance falls substantially, and resistance will increase. Corrosion resistance is low, and after forming membranes on a substrate, it discolors only by neglecting [ about ] it to the atmosphere on the 1st, and becomes a reflection property which is tinged with the yellow taste. And it was corroded by the drug solution used at the time of manufacture of a display, and there was a problem to which reflectance falls substantially.

[0006]The purpose of this invention is to provide the Ag alloy system reflection film which has the high reflectance demanded, for example in plane display devices, such as reflective liquid crystal display and FED, the heat resistance in the inside of a process, corrosion resistance, and the adhesion to a substrate.

[0007]

[Means for Solving the Problem]By considering it as a reflection film which added an element chosen as Ag as a result of inquiring wholeheartedly in order to solve the above-mentioned technical problem, this invention persons improved heat resistance and corrosion resistance, without reducing high reflectance which Ag originally has, found out that adhesion to a substrate was also further improvable, and reached this invention.

[0008]0.2-5at(atom) % That is, this invention is an Ag alloy system reflection film which contains and becomes a remainder real target from Ag about one or more sorts of elements chosen from Ce, Nd, Sm, Gd, Tb, and Dy.

[0009]one or more sorts of elements in which an Ag alloy system reflection film of this invention is chosen from Ti, V, Nb, Cr, Mo, and Mn -- 1 - 10at% -- it may contain.

[0010]

[Embodiment of the Invention]The most important feature of the Ag alloy system reflection film of this invention is in the place which becomes a 0.2-5at% implication and a remainder real target from Ag about one or more sorts of elements chosen from Ce, Nd, Sm, Gd, Tb, and Dy.

[0011]Usually, although the reflectance as a film is high when a reflection film is produced by using pure Ag as a raw material, it is as above-mentioned that there is a problem that reflectance will fall in the process at the time of producing products (for example, liquid crystal display etc.) using the reflection film. So, in this invention, it can be considered as the reflection film which was able to aim at improvement in reflectance from pure Ag depending on the case,

without reducing the reflectance of a reflection film by adding one or more sorts of elements [ a proper quantity of ] chosen as Ag from Ce, Nd, Sm, Gd, Tb, and Dy.

[0012]For example by the manufacturing process of products, such as a liquid crystal display and organic electroluminescence, after forming the reflection film, the process accompanied by a number of times heat-treatment is, and as for Ag reflection film, reflectance falls also according to the heating process in that case. That is, film growth, condensation, etc. by heating take place, and a membrane surface serves as more irregular shape, and a void occurs. And a membrane surface discolors depending on the heated atmosphere, and this also becomes the cause that reflectance falls. In this case, even if it is, the Ag alloy system reflection film of this invention maintains high reflectance also after the process accompanying this heating by adding one or more sorts of elements [ a proper quantity of ] chosen from Ce, Nd, Sm, Gd, Tb, and Dy which were mentioned above to Ag.

[0013]Ce of above-mentioned this invention, Nd, Sm, Gd, Tb, and Dy made its addition and content 0.2 - 5at% in total. This is because sufficient reflectance cannot be maintained and secured less than [ 0.2at% ] if there is no heat-resistant improvement effect by the content and 5at% is exceeded. For obtaining still higher heat resistance and the high reflectance of not less than 95%, 1 - 4at% of content is desirable.

[0014]Maintenance of the reflectance by content of the above-mentioned element seed of this invention or the reason for improvement is not clear. However, since in the case of comparatively low Ag of the melting point the alloying element of Ce, Nd, Sm, Gd, Tb, and Dy which this invention selected tends to form Ag and a compound and it deposits in a grain boundary, this prevents oxidation by Ag intergranular corrosion, raises corrosion resistance, and is considered that high reflectance is maintainable.

[0015]Since the grain growth in a heating process and condensation are controlled when the compound of Ag deposits in a grain boundary, heat resistance improves. And since it becomes a film gestalt of the detailed and smooth surface, decline in reflectance can be controlled. To improve adhesion is considered by the effect that membrane stress is reduced by addition of these element seeds, and the effect of both condensation control.

[0016]Usually, in a sputter film, the element added dissolves by supersaturation all over a base. That is, since an alloying element invades between crystalline lattices at supersaturation, the lattice is confused, and since a motion of a free electron is checked, reflectance falls. However, in the case of this invention in which an alloying element forms grain boundary precipitate, it becomes Ag independent, and a motion of a free electron is not checked, either, but the inside of the Ag grain can maintain high reflectance.

[0017]one or more sorts of elements further chosen from Ti, V, Nb, Cr, Mo, and Mn after the Ag alloy system reflection film of this invention contains one or more sorts of the above-mentioned element seed as indispensable -- 1 - 10at% -- it may contain. By containing these

elements, corrosion resistance improves further and decline in reflectance is controlled.

[0018]Although Ce of this invention, Nd, Sm, Gd, Tb, and Dy tend to form Ag and a compound, intergranular corrosion is controlled by depositing in the grain boundary and it is thought as above-mentioned that this raises corrosion resistance, For example, it may not be enough to secure the corrosion resistance over drug solutions, such as acid used in the manufacturing process of a flat display. It is thought that this [ their ] improves corrosion resistance substantially noting that they deposit in a membrane surface or a grain boundary and protect the whole Ag alloy film, since Ti, V, Nb, Cr, Mo, and Mn which this invention selects have strong acid resistance and do not dissolve easily with the above Ce, Nd, Sm, Gd, Tb, and Dy.

[0019]In addition, Ti, V, Nb, Cr, Mo, and Mn become able [ adhesion with glass or a plastic board ] to improve adhesion with a substrate substantially by it being good and adding to the Ag alloy system reflection film of this invention.

[0020]As for a corrosion-resistant improvement effect, less than [ 1at% ] is [ the content of one or more sorts of elements chosen from Ti, V, Nb, Cr, Mo, and Mn ] insufficient, when 10at% is exceeded, corrosion resistance is excellent, but reflectance will fall substantially. For this reason, as for the content of these elements, it is desirable to consider it as 1 - 10at%. Preferably, it is 1 - 5at%.

[0021]As for the Ag alloy system reflection film of this invention, in order to obtain the stable reflectance, it is preferred to be referred to as 50-300 nm as thickness. A membranous surface shape changes easily that it is less than 50 nm, and when it uses for a plane display device further, in order that light may penetrate, reflectance falls. On the other hand, reflectance does not change a lot that it is the thickness over 300 nm, but when forming a film, it takes time.

[0022]When forming the Ag alloy system reflection film of this invention, it is preferred to use a glass substrate and a Si wafer as a substrate used when forming, for example by sputtering using a target, but. A thin film can be formed by sputtering and what is necessary is for a resin substrate and a metal substrate to be just sufficient.

[0023]

[Example](Example 1) The target material was produced so that it might become substantially the same as that of the target system of an Ag alloy system reflection film, and the target (100 mm in diameter and 5 mm in thickness) was produced by machining. By sputtering using the target, the Ag alloy system reflection film of 200 nm of thickness was formed on the glass substrate or the Si wafer, and the reflectance was measured using the optical reflectometer.

[0024]In order to evaluate reflectance after passing through the manufacturing process as predetermined products, reflectance was again measured for the Ag alloy system reflection film which produced [ above-mentioned ] after heat-treatment by a nitrogen gas atmosphere with a temperature of 250 \*\*. Change of the reflectance by the heat treatment is also combined, and a measurement result is shown in Table 1.

[0025]

[Table 1]

No.	組成(at%)	成膜時 反射率(%)	熱処理後 反射率(%)	反射率差 (%)	区 分
1	Ag	99	88	-11	比較例
2	Ag-0.1Ce	98	92	-6	比較例
3	Ag-0.3Ce	97	95	-2	本発明
4	Ag-1Ce	95	95	0	本発明
5	Ag-0.5Nd	96	95	-1	本発明
6	Ag-1Nd	95	96	1	本発明
7	Ag-7Nd	86	90	4	比較例
8	Ag-0.1Sm	99	92	-7	比較例
9	Ag-0.2Sm	97	95	-2	本発明
10	Ag-0.5Sm	96	96	0	本発明
11	Ag-3Sm	93	96	3	本発明
12	Ag-10Sm	81	84	3	比較例
13	Ag-0.5Gd	96	94	-2	本発明
14	Ag-3Gd	92	96	4	本発明
15	Ag-5Gd	89	94	5	本発明
16	Ag-7Gd	86	88	2	比較例
17	Ag-10Gd	82	91	9	比較例
18	Ag-0.1Tb	98	90	-8	比較例
19	Ag-0.3Tb	96	94	-2	本発明
20	Ag-3Tb	92	95	3	本発明
21	Ag-0.3Dy	97	96	-1	本発明
22	Ag-0.5Dy	95	94	-1	本発明
23	Ag-2Dy	91	94	3	本発明
24	Ag-7Dy	84	90	6	比較例
25	Ag-0.3Nd-2Gd	93	95	2	本発明
26	Ag-0.5Nd-3Sm	90	94	4	本発明
27	Ag-2Tb-2Gd	90	93	3	本発明
28	Ag-3Dy-1Ce	89	94	5	本発明
29	Ag-3Dy-3Tb	83	88	5	比較例
30	Ag-2Gd-4Sm	82	88	6	比較例
31	Ag-4Sm-3Tb	80	86	6	比較例
32	Ag-1Ce-2Nd	91	93	2	本発明

[0026] Although a pure Ag film (No.1) has the reflectance of 99% in the time of membrane formation, reflectance is falling substantially by heat-treatment. As for the Ag alloy film which, on the other hand, contains one or more sorts of elements chosen as Ag from Ce, Nd, Sm, Gd, Tb, and Dy, decline in the reflectance after heat treatment is controlled, and the effect is clear at the addition beyond 0.2at%. However, when the addition increases, there is just little decline in the reflectance after heat treatment, but the reflectance at the time of membrane formation falls, and if 5at% is exceeded, high reflectance will become difficult to get. For this reason, the above-mentioned content of this invention may be 0.2 - 5at% in total. 0.5 - 3at% of the content is desirable for the reflectance of not less than 95% being stabilized.

[0027] (Example 2) Heat-treatment of Example 1 and the conditions was performed on the Ag alloy film which has the formed predetermined presentation, and the reflectance was measured. And the reflectance at the time of neglecting 24h by the environment of the temperature of 80 \*\* and 90% of humidity further was measured. Change of the reflectance by

the environmental test is also combined, and a measurement result is shown in Table 2.

[0028]

[Table 2]

No.	組成(at%)	熱処理後 反射率(%)	環境試験 反射率(%)	反射率差 (%)	区 分
33	Ag	92	86	-6	比較例
34	Ag-1Ce	95	92	-3	本発明
35	Ag-2Nd	95	92	-3	本発明
36	Ag-0.8Sm	95	91	-4	本発明
37	Ag-1Gd	95	93	-2	本発明
38	Ag-3Gd	96	96	0	本発明
39	Ag-5Gd	94	93	-1	本発明
40	Ag-1Tb	95	93	-2	本発明
41	Ag-0.1Dy	92	89	-3	比較例
42	Ag-3Dy	94	93	-1	本発明
43	Ag-3Ti	84	82	-2	比較例
44	Ag-5Mn	81	82	1	比較例
45	Ag-3Cr	83	83	0	比較例
46	Ag-6Cr	81	80	-1	比較例
47	Ag-8Nb	80	80	0	比較例
48	Ag-1Mo	85	82	-3	比較例
49	Ag-2Ce-2Ti	91	90	-1	本発明
50	Ag-3Nd-10Ti	88	88	0	比較例
51	Ag-3Sm-0.5V	94	91	-3	本発明
52	Ag-1Gd-5Nb	91	91	0	本発明
53	Ag-2Gd-11Nb	82	82	0	比較例
54	Ag-3Gd-3Mo	93	92	-1	本発明
55	Ag-0.2Gd-7Mn	90	90	0	本発明
56	Ag-4Gd-1Ti	93	93	0	本発明
57	Ag-0.8Tb-8V	86	86	0	本発明
58	Ag-4Tb-4Ti-2V	86	85	-1	本発明
59	Ag-3dy-2Cr-2Mn	92	92	0	本発明
60	Ag-1Dy-12V-2Ti	82	82	0	比較例
61	Ag-0.5Gd-2Ti-5Mo	88	87	-1	本発明
62	Ag-2Sm-5Ti-10Al	88	88	-1	本発明
63	Ag-3Ce-3Nb-15Al	90	89	-1	本発明

[0029] Reflectance is falling substantially [ a pure Ag film (No.33) ] at the above-mentioned environmental test. In the case of the Ag alloy film (No.43-48) which added chisels, such as Ti and Mn, Ag has just little decline in the reflectance by the above-mentioned environmental test, but it turns out that the reflectance itself is low. To them, the Ag alloy film of this invention has little decline in reflectance also in also after the corrosion resistance by an environmental test evaluates, and it turns out that high reflectance is maintainable.

[0030](Example 3) The following process examinations performed corrosion-resistant evaluation. the substrate [ which formed the Ag alloy film of the presentation in Example 2 ] top of which production and heat treatment were done -- Tokyo -- adaptation -- make OFPR-800 resist was formed with the spin coat. Next, negatives were developed after exposing resist by ultraviolet rays organic alkali developing solution NMD-3 using the photo mask, and after the resist pattern was produced and immersed in dilute hydrochloric acid for 30 seconds, the



reflectance of the immersion portion was measured again. Change of the reflectance by the process examination is also combined, and a measurement result is shown in Table 3.

[0031]

[Table 3]

No.	組成(at%)	熱処理後 反射率(%)	プロセス試験 反射率(%)	反射率差 (%)	区 分
33	Ag	92	74	-18	比較例
34	Ag-1Ce	95	90	-5	本発明
35	Ag-2Nd	95	91	-4	本発明
36	Ag-0.8Sm	95	90	-5	本発明
37	Ag-1Gd	95	90	-5	本発明
38	Ag-3Gd	96	92	-4	本発明
39	Ag-5Gd	94	92	-2	本発明
40	Ag-1Tb	95	91	-4	本発明
41	Ag-0.1Dy	92	86	-6	比較例
42	Ag-3Dy	94	91	-3	本発明
43	Ag-3Ti	84	80	-4	比較例
44	Ag-5Mn	81	80	-1	比較例
45	Ag-3Cr	83	79	-4	比較例
46	Ag-6Cr	81	79	-2	比較例
47	Ag-8Nb	80	80	0	比較例
48	Ag-1Mo	85	81	-4	比較例
49	Ag-2Ce-2Ti	91	91	0	本発明
50	Ag-3Nd-10Ti	88	88	0	比較例
51	Ag-3Sm-0.5V	94	91	-3	本発明
52	Ag-1Gd-5Nb	91	91	0	本発明
53	Ag-2Gd-11Nb	82	81	-1	比較例
54	Ag-3Gd-3Mo	93	92	-1	本発明
55	Ag-0.2Gd-7Mn	90	89	-1	本発明
56	Ag-4Gd-1Ti	93	93	0	本発明
57	Ag-0.8Tb-8V	86	86	0	本発明
58	Ag-4Tb-4Ti-2V	86	86	0	本発明
59	Ag-3dy-2Cr-2Mn	92	91	-1	本発明
60	Ag-1Dy-12V-2Ti	82	82	0	比較例
61	Ag-0.5Gd-2Ti-5Mo	88	88	0	本発明
62	Ag-2Sm-5Ti-10Al	89	89	0	本発明
63	Ag-3Ce-3Nb-15Al	90	89	-1	本発明

[0032] Reflectance is falling substantially [ a pure Ag film (No.33) ] at the above-mentioned process examination. In the case of the Ag alloy film (No.43-48) which added chisels, such as Ti and Mn, Ag has just little decline in the reflectance by the above-mentioned process examination, but it is as having stated that the reflectance itself is low. decline in the reflectance according [ the Ag alloy film of this invention which added rare earth element:Ce of the specified quantity, Nd, Sm, Gd, Tb, and Dy to Ag to them ] to a process examination -- it is also -- then, even if it is, the reflectance of not less than 90% is maintained. And it turns out that the Ag alloy film of this invention which added transition metal:Ti of the specified quantity, V, Nb, Cr, Mo, and Mn further can maintain high reflectance after a process examination.

[0033](Example 4) Next, membranous adhesion is evaluated. Adhesion with the substrate of the film was measured with the substrate which formed and produced the Ag alloy film of the

presentation in the Example 2. When Scotchtape was stuck on a membrane surface and a tape was specifically torn off in the direction of 45 degrees of slant, the area which remained on the substrate was expressed with the area rate per 20-cm<sup>2</sup>, and was evaluated as adhesion power. A result is shown in Table 4.

[0034]

[Table 4]

No.	組成(at%)	密着力(%)	区 分
33	Ag	80	比較例
34	Ag-1Ce	86	本発明
35	Ag-2Nd	87	本発明
36	Ag-0.8Sm	85	本発明
37	Ag-1Gd	85	本発明
38	Ag-3Gd	87	本発明
39	Ag-5Gd	89	本発明
40	Ag-1Tb	86	本発明
41	Ag-0.1Dy	82	比較例
42	Ag-3Dy	86	本発明
43	Ag-3Ti	97	比較例
44	Ag-5Mn	95	比較例
45	Ag-3Cr	97	比較例
46	Ag-6Cr	99	比較例
47	Ag-8Nb	99	比較例
48	Ag-1Mo	92	比較例
49	Ag-2Ce-2Ti	95	本発明
50	Ag-3Nd-10Ti	97	比較例
51	Ag-3Sm-0.5V	85	本発明
52	Ag-1Gd-5Nb	95	本発明
53	Ag-2Gd-11Nb	99	比較例
54	Ag-3Gd-3Mo	95	本発明
55	Ag-0.2Gd-7Mn	93	本発明
56	Ag-4Gd-1Ti	93	本発明
57	Ag-0.8Tb-8V	92	本発明
58	Ag-4Tb-4Ti-2V	94	本発明
59	Ag-3dy-2Cr-2Mn	95	本発明
60	Ag-1Dy-12V-2Ti	95	比較例
61	Ag-0.5Gd-2Ti-5Mo	96	本発明
62	Ag-2Sm-5Ti-10Al	99	本発明
63	Ag-3Ce-3Nb-15Al	95	本発明

[0035]As compared with the pure Ag film (No.33), as for the Ag alloy film of this invention which added Ce of the specified quantity, Nd, Sm, Gd, Tb, and Dy to Ag, adhesion is improved substantially. And in the Ag alloy film of this invention which also added Ti of the specified quantity, V, Nb, Cr, Mo, and Mn, it turns out that the further outstanding adhesion is acquired.

[0036]

[Effect of the Invention]If it is this invention, it is possible to obtain the Ag alloy system reflection film which has improved high reflectance, a resistance to environment and chemical resistance, and adhesion with a substrate. Therefore, it is useful to plane display devices, such as reflective liquid crystal display in which the low power consumption used for a Personal

Digital Assistant etc. is demanded, and industrial value is high.

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[Translation done.]